

SULFUR IN HEAVY OILS, OIL SANDS AND OIL SHALES

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INTRODUCTION

Sulfur, after carbon and hydrogen, is often the most abundant element in fossil organic materials, whereas in biological tissues and their degradation products oxygen and nitrogen usually are more abundant than sulfur. In rare cases, the sulfur content on a weight basis even exceeds the hydrogen content. Nevertheless, sulfur in petroleum appears to be non-essential, *i.e.*, it is not a necessary component for the formation of petroleum and related bitumens because some of these materials contain only trace amounts.

The chemistry of sulfur in fossil fuels and related materials is of interest for two major reasons: 1) For its behavior during processing and in applications: It can cause problems in processing and has deleterious effects on the environment in many applications, and 2) For its geochemical significance, *i.e.*, for understanding processes which determine its abundance, distribution, and chemical combination (forms) during both the formation and alteration of fossil organic materials in geologic environments.

Emphasis in this paper is on the second area -- the geochemistry of sulfur in crude oils, oil sands and related materials. The first section of this paper briefly summarizes some of the factual knowledge concerning the abundance and forms of sulfur in these materials, especially in crude oils. Following this is a more speculative section discussing opinions and our understanding of the geochemical processes believed to control and modify the abundance and forms of sulfur. In spite of much research and a great body of factual knowledge, many important questions are still debated and diverse views will be found in the literature.

THE NATURE AND ABUNDANCE OF SULFUR IN FOSSIL FUELS

Crude oils and bitumens vary in sulfur content from less than 0.05 to more than 14%, although relatively few produced crude oils contain more than 4% sulfur. Most oils contain from 0.1 to 3% sulfur. Similar variations in sulfur content are found in lignites, coals and the organic matter (kerogen) in oil shales and other sedimentary rocks.

Comprehensive reviews concerning sulfur and sulfur compounds in petroleum have been given by Dean and Whitehead (1), Rall *et al.* (33) and Zobell (43). Drushel also reviewed sulfur compound types in petroleum with emphasis on analytical methods (12). Challenger's monograph on the organic chemistry of sulfur (6) includes much of the early work on sulfur in fossil fuels as well as aspects of biochemistry and biogeochemistry of sulfur. The biogeochemistry of sulfur has been more recently summarized by Orr (28). Monographs are available also on microbiological processes in the formation of sulfur deposits (19) and on the biochemistry of inorganic sulfur compounds with emphasis on microbiology (35).

Hydrogen sulfide* and elemental sulfur dissolved in crude oils usually are a very minor portion of the total sulfur if they are present at all (24,

* Oils containing detectable amounts of hydrogen sulfide or mercaptans (thiols) are referred to as "sour crudes". High sulfur oils without these components should not be called sour (24). However, hydrogen sulfide in a sour crude oil is easily oxidized by air to elemental sulfur during surface handling and processing. Later, during thermal treatment, H₂S may form again from thermal reactions of the elemental sulfur with other components and/or from thermal decomposition of unstable sulfur compounds.

It is reasonable that the sulfurization of organic matter can occur at any stage in the geological history of a given material if proper conditions prevail. However, many advocates for a late introduction apparently do not appreciate the magnitude of sulfur incorporation into initial sedimentary organic matter in certain environments. For example, humic acids extracted from young marine sediments contain from 0.8 to 6 %S, and these acidic polymeric materials make up from 20 to 60% of the organic matter in many sediments (26). Humic acids may be considered major precursors of kerogen which in turn can be the major precursor of petroleum (41).

Gransch and Posthuma (16) conclude that most of the sulfur in crude oils originates from organically combined sulfur in the kerogen of source rocks, and therefore the major sulfur compounds and hydrocarbons are formed together. They give a number of examples illustrating that high-sulfur kerogens produce high-sulfur oils and vice versa. They also concluded from laboratory experiments that more sulfur compounds are formed during the early stages of oil generation from a given kerogen than during the later stages of its decomposition. Thus the sulfur content of an oil is a function of both the initial sulfur content of its source kerogen and its state of maturation or evolution. I believe these conclusions are essentially correct and are accepted by a large number of geochemists. Nevertheless, there are subsequent changes and alterations in oils after they are formed, possibly during their migration, and after their accumulation in reservoirs. Many questions remain about the nature and importance of these effects. Evidence of late sulfurization and competing desulfurization of oils during thermal maturation in some high temperature reservoirs has been demonstrated (27, 29), but since this does not relate directly to heavy oils it will not be discussed.

Studies of sulfur isotope ratios ($^{34}\text{S}/^{32}\text{S}$)* have contributed to our understanding of the origin of sulfur in petroleum and support the view for its early incorporation into oil precursor materials. These studies indicate that a large portion of the sulfur has been derived from reduced sulfur (H_2S and/or S^0) showing a typical isotopic fractionation attributed to microbial reduction of sulfate under conditions where the supply of sulfate is not largely reduced (i.e., in an open system) (27, 36, 37, 38).

It has been established that the $\delta^{34}\text{S}$ values of sea water have fluctuated considerably with geologic periods (17, 37, 38) and that $\delta^{34}\text{S}$ values of sulfur in crude oils show parallel fluctuations with geologic age but are commonly 15 ± 5 ‰ lighter isotopically than sea water sulfate of the same age. These observations are most reasonably explained by isotopic fractionation during microbial reduction of sea water sulfate at the time of sediment deposition. The H_2S and/or S^0 thus formed became incorporated into sedimentary organic matter with retention of its isotopic ratio. Later with the formation of petroleum by thermal processes resulting from deeper burial, the sulfur compounds formed with the hydrocarbons retain the isotopic ratio reflecting the original isotopic fractionation.

The amount of sulfur initially incorporated into sedimentary organic matter may be expected to be determined by 1) the abundance of sulfate in the water, 2) the Eh of the environment near the sediment-water interface which is one of the controls on the intensity of microbial sulfate reduction, 3) the

* Sulfur isotope ratios are reported as deviations (δ - values) in parts per mil (‰) from a standard according to the relationship:

$$\delta^{34}\text{S}(\text{‰}) = \left[\frac{^{34}\text{S}/^{32}\text{S}_{\text{(sample)}}}{^{34}\text{S}/^{32}\text{S}_{\text{(standard)}}} - 1 \right] \times 1000$$

The standard is troilite from the Canyon Diablo meteorite which has an absolute $^{34}\text{S}/^{32}\text{S}$ ratio accepted as 0.0450045. The $\delta^{34}\text{S}$ values can be either positive or negative with respect to the standard.

nature and abundance of organic matter which not only affects the extent of sulfate reduction but also influences the degree to which reduced sulfur species will become organically combined through reactions with reactive functional groups, and 4) the abundance of iron or other elements (cations) which compete with organic matter for the reduced sulfur. Thus, with the variations which can occur in these factors, and accepting the concept that sulfur in the sedimentary organic matter is the major source of sulfur in any oil derived therefrom, it is easy to understand that crude oils as initially formed can have wide variations in sulfur content. These variations, therefore, reflect conditions of the initial sedimentary environments.

There is another school of thought which would attribute a large part of the sulfur in crude oils to late sulfurization resulting from microbial sulfate reduction occurring in relatively shallow petroleum reservoirs (2, 8, 14). Microbial sulfate reduction certainly has been demonstrated in petroleum reservoirs (1, 2, 3, 8, 14) and as a result oil field waters are often very deficient in sulfate. However, the extent to which the resulting hydrogen sulfide reacts with the oil is difficult to evaluate. It is probably variable and often negligible. Petroleum no longer contains the abundance of reactive function groups which existed in younger organic materials in the early source environments. Its sulfurization is expected to be very slow and possibly negligible in low temperature reservoirs where microbial activity occurs. For example, Gransch and Posthuma (16) illustrate that there is not a dramatic difference in sulfur content between "flank oils" and "cap-rock oils" associated with Gulf Coast salt domes especially if any dissolved elemental sulfur is discounted in the cap-rock oils. Sulfate reduction is known to have been very active in many of the cap-rocks as evidenced by deposits of elemental sulfur and secondary calcite (14).

Although it is difficult to extrapolate laboratory experiments to geologic conditions, the experiments reported by Bestougeff and Combaz are of interest (5). They demonstrated great differences in the ease of sulfurization of different organic materials and the relative inertness of oils and oil fractions. Low boiling fractions are very inert but high boiling fractions and residues (fractions enriched in asphaltic heteroatomic and aromatic compounds) are more reactive to sulfurization by hydrogen sulfide, elemental sulfur and polysulfides. These observations support the view that sulfurization of oils in low temperature reservoirs is not easy and that any sulfur which may be introduced should be largely in the heavy ends of the oil.

B. Effects of Biodegradation and Water-Washing on Sulfur in Fossil Fuels

These crude oil alteration processes have been adequately discussed in the literature (1, 2, 8, 13, 32, 42) and only selected aspects can be reviewed here. These processes are discussed together because they commonly occur together in oil reservoirs. An active aquifer facilitates both processes.

Water-washing refers to the extractive removal of crude oil components which, of course, depends on their solubility in the aqueous phase. Biodegradation refers to the oxidation of crude oil components by bacteria and therefore has biochemically controlled selectivity which may be different for various microbial communities.

Microbial activity has an upper temperature limit whereas water-washing does not. Nevertheless, active aquifers associated with petroleum reservoirs are commonly shallow and temperatures are therefore sufficiently low for microbial activity. The aquifer may supply oxygen for aerobic bacteria and/or sulfate for anaerobic sulfate reducing bacteria.

Microbial utilization of hydrocarbons by aerobic microorganisms has been known for many years by microbiologists (3, 8, 40), but the utilization of hydrocarbons by anaerobic microorganisms is debated and is difficult to demonstrate in the laboratory (8). Nevertheless, field studies and natural observations provide strong evidence of microbial reduction of sulfate (an anaerobic process) in many situations where petroleum hydrocarbons are the most likely organic substrate available (8, 14, 19, 32). Furthermore, there is ample evidence that in many such cases secondary calcite has been formed which has carbon isotope ratios indicating that its carbon must have been derived from the oxidation of

hydrocarbons (14). It must be concluded that microbial oxidation of crude oils in the subsurface does occur and may involve both aerobic and anaerobic microorganisms.

Interest in biodegradation of crude oils in reservoirs received a new stimulus by the rather definitive study of the Bell Creek Field reported by Winters and Williams in 1969 (42). In this case the biodegradation was attributed largely to aerobic microorganisms because of relationships between changes in oil composition and locations of wells in the field. Shallower oils closer to the aquifer outcrop were more degraded than deeper oils further from the outcrop. Variations of oxygen with distance from the outcrop were considered to be a controlling factor.

Most recently, Philippi (32) has taken a strong position suggesting that all "primary" crude oils are paraffinic, and that all "naphthenic" crude oils are the result of microbial attack on the primary oils. He also believes that anaerobes are effective in these transformations. Bailey et al. (1) also assume that bacteria can metabolize most types of hydrocarbons including aromatics and naphthenes although n-alkanes are most readily attacked. Thus, it has become common for geochemists to accept certain criteria as evidence of microbial degradation. Major gross criteria are a relative decrease in n-alkanes, an increase in density (decrease in API gravity), and an increase in cycloalkanes, aromatics and heteroatomic compounds (N, S, and O compounds). Isoprenoids, e.g., pristane and phytane, initially show an apparent increase relative to n-alkanes because of their slower utilization but subsequently they decrease relative to cycloalkanes and other compounds. Philippi and others have discussed additional criteria based on the relative amounts of various compound types and/or isomer ratios. Unfortunately, no absolutely stable marker is known which would allow assessment of absolute changes rather than relative changes.

Our interest in this paper centers mainly on the increase in sulfur content of oils during biodegradation. We subscribe to the thesis that the increase in sulfur content occasioned by biodegradation is largely due to losses of non-sulfur compounds rather than to an introduction of additional sulfur. Some consequences of this thesis and evidence for its support are given below. However, it should be clear that definitive data are still lacking and the problem needs further study.

In reported suites of oils believed to represent undegraded and biodegraded oils from a common source, the sulfur content often increases by a factor of 2 or 3 (1, 2, 13, 16)*; the factor may be greater in very heavy asphalts and tar sands but definitive data are not available to my knowledge. If this increase is merely a concentration of sulfur compounds from the relative loss of non-sulfur compounds, it requires that 50 to 70% of the initial oil must be destroyed. In most cases this is greater than that possible from selective removal of n-alkanes alone and therefore appreciable losses of iso- and cyclo-alkanes and aromatics are required. If some of the sulfur compounds are also utilized, then, of course, losses must be even greater. In the absence of an absolute marker or complete material balance information, we cannot draw a final conclusion. Nevertheless, such large losses may be possible.

The limited data on sulfur isotope ratios for Midway-Sunset oils shown in Fig. 8 are consistent with the above suggestion that the sulfur increase during biodegradation does not necessarily involve the introduction of new sulfur formed by microbial reduction of sulfate. These three oils, which vary in sulfur content from 0.51 to 1.08% and in API gravity from 26.1 to 15.1°, have essentially identical sulfur isotope ratios. This suggests that either little or no new sulfur was introduced or the rather unlikely coincidence that the sulfur introduced

* It is of some interest that the increase in %N and in optical activity appears to be of the same order of magnitude.

had the same sulfur isotope ratio as that in the original oil. Further isotopic studies of this type including measurements on associated hydrogen sulfide and sulfates should help delineate situations where sulfurization does or does not occur during biodegradation of crude oils.

Another bit of evidence supporting the above position may be found in the homogeneity of sulfur isotopes in crude oils. Monster (23) demonstrated that sulfur isotope ratios were almost identical in the asphaltenes and various chromatographic fractions from a few crude oils. If the conclusions of Bestougeff and Combaz (5) are valid, one would expect the newly introduced sulfur to be mostly in the more polar and higher molecular weight fractions. Therefore, a homogeneous distribution of sulfur isotope ratios would not be expected unless the reacting hydrogen sulfide and/or elemental sulfur had the same isotope ratios as that of the sulfur initially in the oils. The oils examined by Monster are regarded as biodegraded oils. They included two of the Mission Canyon (MC-5) oils studied by Bailey *et al.* (2) and the Athabasca oil sand. Only a few oils have been examined for homogeneity of sulfur isotopes. Another case is the Fourbear oil from the Big Horn Basin. In this case very little difference in sulfur isotope ratios was found in distillations cuts and the distillation residue (see Fig. 11 in reference 27). This is one of the heaviest and probably most biodegraded oils in the Big Horn Basin.

A third argument for our thesis may be the fact that biodegraded heavy oils and tar sands do not necessarily have a high sulfur content. This was emphasized by Clair *et al.* (7) in reporting on the heavy oils of the Emerald Field and some nearby but deeper light oils. The light oils with only about 0.12% S were concluded to be the type of oil which during biodegradation in the Emerald Field produced heavy oils with about 0.8% S. These authors make the following statement (Translated from French text): We are led to suppose that the sulfur enrichment in the course of biological degradation is largely only an effect of concentration of the products not consumed by microorganisms, and does not imply any appreciable introduction of sulfur from outside.

C. Sulfurization and Desulfurization Processes in High Temperature Reservoirs

Changes in abundance and forms of sulfur which occur during thermal maturation of crude oils are important for understanding the geochemistry of sulfur in oils, bitumens, pyrobitumens and natural gases. However, because these processes have little to do with heavy oils or the other subject materials except by way of contrast, we simply mention their existence and reference discussions dealing with them (27, 29, 30).

In high temperature reservoirs desulfurization always accompanies thermal maturation of oils. The sulfur is lost partly as hydrogen sulfide and partly as precipitated reservoir bitumens or pyrobitumens. Under certain conditions hydrogen sulfide may accumulate and sulfurization may compete with desulfurization. This can lead to a dynamic steady-state sulfur system. These interesting high temperature processes are important in understanding deep oils, condensates and natural gases. They can lead to gases unusually rich in hydrogen sulfide and condensates unusually rich in thiols.

SUMMARY AND CONCLUSION

We have briefly reviewed the geochemistry of sulfur as it relates to crude oils and other fossil fuels.

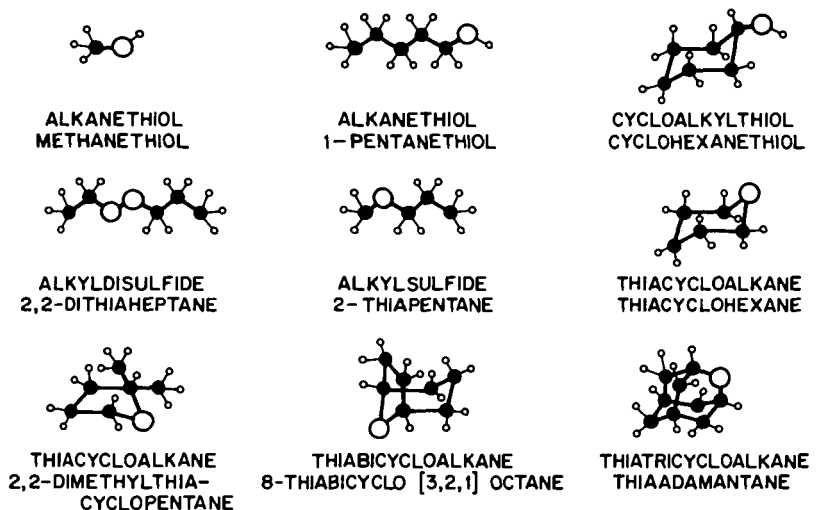
Heavy oils and asphaltic oil sands are believed to have been formed largely by biodegradation of lighter oils. The sulfur content of a heavy oil and/or oil sand is believed to be determined largely by the sulfur content of the undegraded precursor oil and the extent of biodegradation which involves a preferential removal of non-sulfur components. New sulfur probably is not added to the residual oil during biodegradations but its concentration is increased mainly because of the removal of other components.

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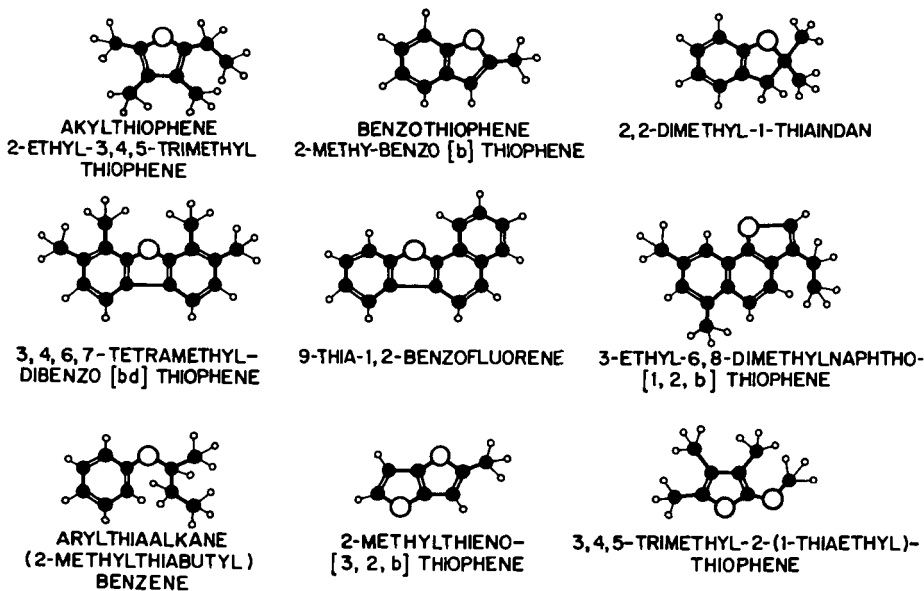
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EXAMPLES OF ALIPHATIC SULFUR COMPOUNDS IN PETROLEUM

Figure 1.



EXAMPLES OF AROMATIC SULFUR COMPOUNDS IN PETROLEUM

Figure 2.

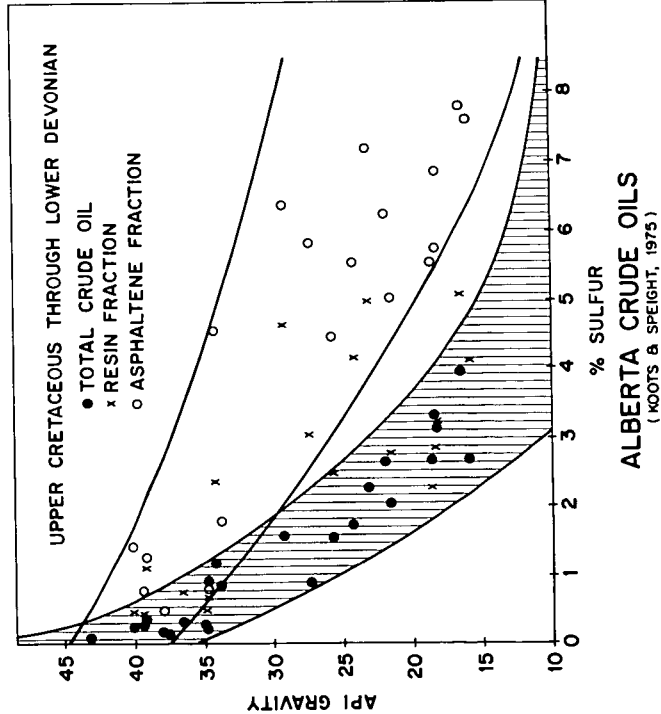


Figure 3.

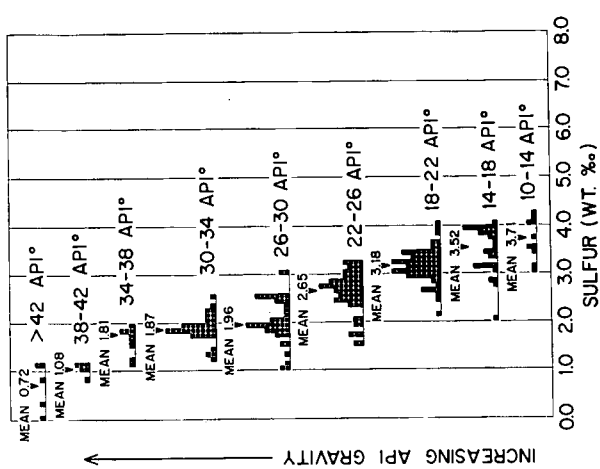


Figure 4.

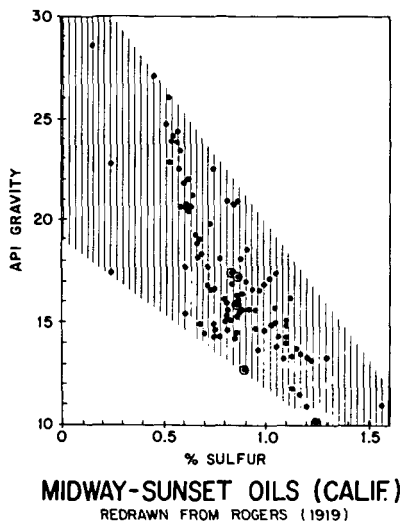


Figure 5.

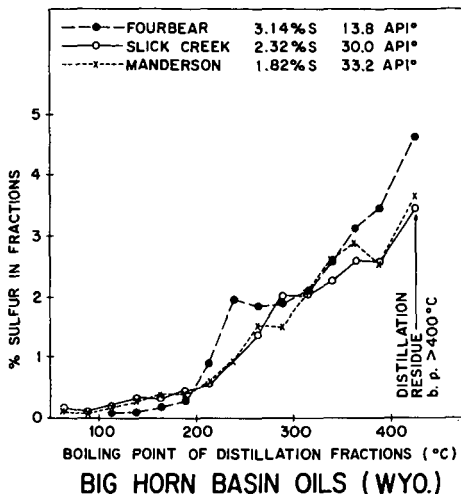
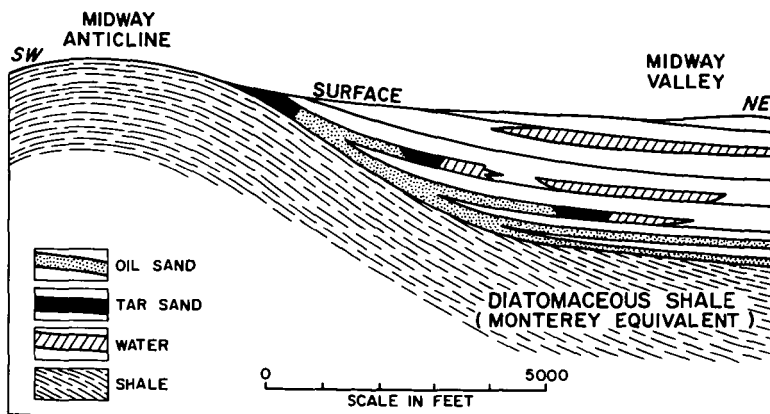
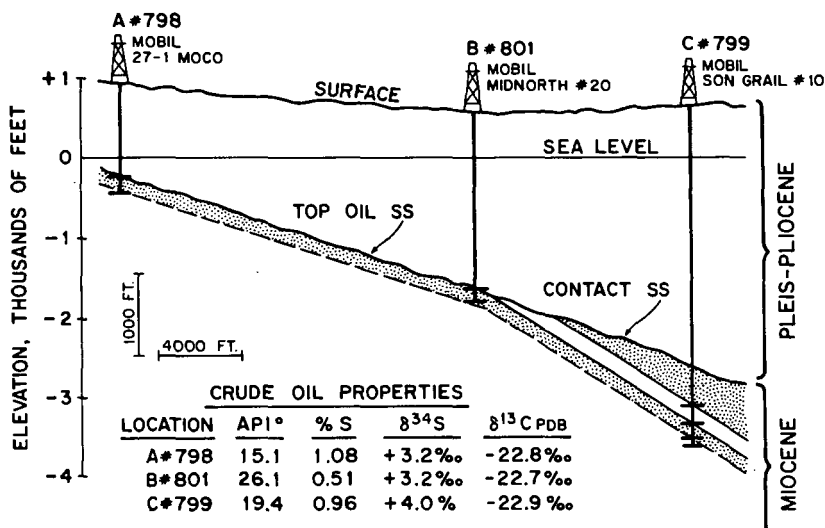


Figure 7.



**DIAGRAM SHOWING RELATIONS OF OIL, TAR & WATER ZONES
 IN VICINITY OF FELLOWS (MIDWAY-SUNSET FIELD)**
 FROM ROGERS (1919) FIG. 13, p. 115

Figure 6.



CROSS SECTION OF MIDWAY-SUNSET FIELD

Figure 8.